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A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing compounds

R. Koppmann[1,*], **K. von Czapiewski**[1], **and J. S. Reid**[2]

[1]Institut für Chemie und Dynamik der Geosphäre, Institut II: Troposphäre, Forschungszentrum Jülich, Jülich, Germany
[2]Marine Meteorology Division, Naval Research Laboratory, Monterey, CA, USA
[*]now at: Applied Biosystems, Darmstadt, Germany

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Correspondence to: R. Koppmann (r.koppmann@fz-juelich.de)

Abstract

Biomass burning is the burning of living and dead vegetation. Ninety percent of all biomass-burning events are thought to be human initiated. Human induced fires are used for a variety of "applications" such as agricultural expansion, deforestation, bush control, weed and residue burning, and harvesting practices. Natural fires are grassland and forest fires mainly induced by lightning. It is estimated that 8700 Tg of dry matter/year are burnt each year in total. Emissions from biomass burning include a wide range of gaseous compounds and particles that contribute significantly to the tropospheric budgets on a local, regional, and even global scales. The emission of CO, CH_4 and VOC affect the oxidation capacity of the troposphere by reacting with OH radicals, and emissions of nitric oxide and VOC lead to the formation of ozone and other photo oxidants. For a large number of compounds biomass burning is one of the largest single sources in the troposphere, especially in the tropics. Biomass-burning emissions play an important role in the biogeochemical cycles of carbon and nitrogen. Following the first systematic investigations on fire emissions in laboratory experiments in the 1960's, the last 20 years saw an increasing number in studies on biomass-burning emissions in various ecosystems. Recently, our knowledge of the emissions of gaseous compounds in the troposphere from fires has increased considerably. This manuscript is the first of four describing the properties biomass burning emissions. The properties of biomass-burning particles are discussed in part II and III of this review series which have been recently published, and their direct radiative effects are in part IV. This paper focuses on the review of emission ratios and emission rates of carbon monoxide, methane, volatile organics, and nitrogen containing compounds and should not be seen as a review of global emission estimates, even though we discuss the implications of our results on such studies.

ACPD

5, 10455–10516, 2005

1. Introduction

Biomass burning is a significant global source of gaseous and particulate matter emissions to the troposphere. Emissions from biomass burning are known to be a source of greenhouse gases such as carbon dioxide, methane and nitrous oxide. Beyond that, biomass burning is a considerable source of chemically active gases such as nitric oxide, carbon monoxide and volatile organic compounds (VOC). This is especially true in tropical and subtropical regions (Crutzen et al., 1979, 1985; Greenberg and Zimmerman, 1984; Zimmerman et al., 1988; Bonsang et al., 1991; Rudolph et al., 1992, 1995; Koppmann et al., 1997; Andreae et al., 1997). Due to transport, these emissions not only have a significant impact on the budget of organic trace gases in the tropical marine atmosphere (Koppmann et al., 1992; Swap et al., 1996), but also in the remote troposphere (Andreae et al., 1994, 2001; Pickering et al., 1996; Chatfield et al., 2002; Pak et al., 2003; Honrath et al., 2004). Moreover, owing to their impact on the photochemical ozone formation, organic trace gases influence the budget of tropospheric ozone (Fishman et al., 1990; Helas et al., 1995a; Thompson et al., 1996a; Poppe et al., 1998; Schultz et al., 1999). Besides their impact on global atmospheric chemistry and biogeochemical cycles, the formation of ozone and other photo oxidants due to the turnover of VOCs from biomass burning may have a significant impact on the regional environment and on the health of the population living in the vicinity of biomass burning events as well as thousands of miles away (Jaffe et al., 2004). Moreover, biomass-burning emissions are also a source of a number of halogenated compounds such as methyl chloride and methyl bromide that are long-lived enough to destroy ozone in the stratosphere.

Rising populations, especially in the third-world countries, will lead to a considerable change in land use and increased exploitation of biofuel as an energy source. This will result in more biomass-burning events in the future and probably in a shift of those areas where biomass burning repeatedly occurs. The gaseous emissions from these fires will have an impact on the chemical composition of the atmosphere, the formation

ACPD
5, 10455–10516, 2005

of photo oxidants and thus on air quality at least on a regional scale. This will not only increase greenhouse gases in the atmosphere but also have an influence on the self-cleaning capacity of the troposphere. Therefore, there is an increasing need of information on the composition of biomass-burning emissions and the effects of these emissions on the atmosphere. This knowledge is essential to integrate atmospheric phenomena with those of the Earth's surface and biosphere. Biomass burning is certainly among the most important aspects to climate change (cf. Andreae et al., 2005). In this paper we review the wide spread literature regarding gaseous emissions of biomass burning to give an overview of the present state of knowledge, to identify gaps in the community literature and give recommendations for future research. The paper focuses on the review of emission ratios and emission rates and should not be seen as a review of global emission estimates, even though we discuss the implication of our results on such studies.

2. Processes of combustion and emission

The biomass combustion processes and its relation to resulting emissions of gaseous compounds have been described in detail elsewhere (e.g., Chandler et al., 1983; Nussbaumer, 1989; Marutzky, 1991; Lobert and Warnatz, 1993) and need only be summarized here briefly. The burning of vegetation is a combination of different physical and chemical processes and is generally divided into three basic combustion phases: ignition, flaming and smoldering. During the ignition phase, small pieces of vegetation, such as leaves, needles, and twigs, are directly set alight by adjacent ignited biomass. Larger pieces, such as branches, undergo radiative heating culminating in combustion. The length of the ignition phase depends greatly on the properties of the fuel, such as water content, density, and size. Since evaporating water vapor is very effective in maintaining relatively low temperatures and transporting heat away, most of the water must be out-gassed from the fuel before ignition can occur. During this initial heating period, large quantities of highly volatile organics, such as aromatic and ether

ACPD
5, 10455–10516, 2005

extractives, are also released.

Once the fuel is sufficiently dry, combustion can proceed from the ignition phase to the flaming phase (~600 K if there is a preexisting flame and ~900 K for spontaneous combustion, Chandler et al.,1983). During flaming combustion, hydrocarbons are volatized through a char layer from the thermally decomposing biomass, mixed with air, and rapidly oxidized in a flame. The principle fuel components in the flaming phase are:

1. Cellulose and hemicellulose: A complex carbohydrate and polysaccharide, respectively, that are the main constituents of the cell wall (50–65%),
2. Lignin: A complex noncarbohydrate polymer that binds to cellulose fibers together and strengthens the cell walls (16–35%),
3. Extractives: Organic species that are not part of the cellular structure of the biomass and can be dissolved or outgassed out (0.2%–15%),
4. Trace minerals.

Products of a complete combustion are carbon dioxide and water. Incomplete combustion leads to the emission carbon monoxide and of a large variety of organic compounds (Nussbaumer, 1989). The composition and amount of emissions are determined by the course of the fire, oxygen supply, temperature and elementary composition of the fuel (Marutzky, 1991). In the exhaust plumes of biomass burning, volatile organic compounds from both cracking of organic fuel material and synthesis from organic compounds in the flame have been detected. Plant matter contains a large amount of volatile organic material. Using the same amount of fuel, combustion of wood leads to significantly higher emissions of VOC than combustion of natural gas, oil or coal. Furthermore, moisture content and composition vary more in wood than in all other fuel materials. Owing to the complex structure of wood and the intricate chemistry within the flame it is not possible nor practical to determine all chemical processes in detail. A prediction of the emissions of gaseous compounds during combustion from

ACPD
5, 10455–10516, 2005

first principles alone is almost impossible due to the complexity of processes of mixing in the flames, cracking and oxidation reactions.

During the process of drying, the morphological and macromolecular structure of the biomaterial changes. Wood material is cracked into hundreds of different gaseous products and solid products consisting mainly of charcoal.

Gaseous compounds can be separated in primary and secondary emissions products. During a low temperature phase (typically <100°C) the poly-saccharides and functional groups of hemicellulosis and lignin decompose. In this stage of the fire methanol, light aldehydes, formic and acetic acid are the dominant emissions (Marutzky, 1991). Above 220°C the polymer structure of the wood is decomposed. In this stage of the fire about 80% of the material is thermally decomposed and a large amount of gaseous compounds is emitted. The organic composition of the emissions is determined by the temperature and the rate of temperature increase. At temperatures of 250–500°C methane, aldehydes, methanol, furanes and aromatic compounds such as benzene, toluene, ethyl benzene and phenol are emitted. The duration of this phase increases with increasing moisture content and increasing amount of the fuel material.

The emitted gases, mostly oxygenated compounds, will be burnt more or less completely in presence of oxygen leading to the formation of stable volatile organic compounds. During the flaming phase of a fire the gaseous compounds are oxidized further in radical reaction chains that are to some extent similar to the VOC chemistry in the troposphere. In flames with excess of oxygen the reactions are initiated by OH radicals, in flames with oxygen deficiency chemical reactions are initiated by the H radical. In the latter situation synthesis reactions are observed due to high concentrations of methyl radicals. In these reactions higher molecular weight hydrocarbons are formed.

Aromatic compounds are formed by chemical reaction in the flames. Aliphatic compounds are added and cyclisized to form aromatics. The amount of aromatic compounds is determined by the amount of aromatic precursors in the fuel material and the flame temperatures. The ratio of the primary emitted to secondary formed aro-

ACPD
5, 10455–10516, 2005

matic compounds is not yet known.

Oxygenated aliphatic compounds are typically C_1- or C_2-hydrocarbons. This is due to the high rate coefficients for the oxidation of alkyl radicals with more than two carbon atoms. They decompose rapidly by the elimination of an alkene. The emission of oxygenated compounds depends significantly on the temperature of pyrolysis. Maximum emission occurs at 350°C. More than 50% of the emitted aldehydes are formaldehyde and acetaldehyde (Struschka, 1993; Nussbaumer, 1989). The use of moist fuel material increases the amount of emitted aldehydes.

The smoldering phase is characterized by flameless combustion (solid phase oxidation) of the charcoal. Charcoal consists of approx. 90% carbon, 5% oxygen and 3% hydrogen. Therefore, the formation rate of volatile organic compounds during this phase is low. But since there is no flame there is little subsequent loss leading to a relatively high emission rates of organic compounds in this stage of the fire. The predominate emitted compound is carbon monoxide. Since the emission rates of all of the products of incomplete combustion emission tend to be correlated (e.g., Ferek et al., 1998), CO is often taken as a surrogate for hydrocarbons and particulate carbon.

3. Summary of "biomass burning equations"

The emission of a specific compound depends on at least two important parameters, the amount of material and the area that is burning. Both parameters are of course dependent on each other via the fuel load per unit area. Therefore, an estimate of the impact of emissions from biomass burning on the atmosphere requires the knowledge of either the total emission of a compound per unit area by a specific fire or the total emission of a compound per unit mass of the burnt material. The total emission of any species n per unit area (n_{te} in g m^{-2}) by a specific fire can be expressed linearly as

$$n_{te} = m_f \cdot f_c \cdot c_f \cdot \langle EF_n \rangle \quad (1)$$

ACPD
5, 10455–10516, 2005

where m_f is the amount of fuel mass available for combustion in kg m^{-2}, f_c is the mass fraction of carbon in the fuel, c_f is the combustion factor (fraction of that mass combusted during the coarse of a fire), and $<EF_n>$ is the combustion averaged *emission factor* for species n in grams of n produced per kg carbon burned averaged over the fire. Of these terms, m_f, and f_c are direct observables, although over large areas, however, the fuel load is highly uncertain. The variable c_f can also be measured post fire. The emission factor, however, is the most variable and on a fire-by-fire basis is the least known.

Over the past 20 years, emission factors have been measured almost exclusively using the Carbon Mass Balance (CMB) method of Ward et al. (1982). The underlying premise of this method is that all of the carbon combusted in a fire is emitted into the measurable portions of a smoke plume in five forms: CO_2, CO, CH_4, non-methane hydrocarbons, and particulate carbon in smoke particles. The emission factor of a species, n, is then calculated from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume:

$$EF_n = \frac{[n]}{[\mathrm{C}]_{\mathrm{CO_2}} + [\mathrm{C}]_{\mathrm{CO}} + [\mathrm{C}]_{\mathrm{CH_4}} + [\mathrm{C}]_{\mathrm{NMHC}} + [\mathrm{C}]_{pc}} \quad (2)$$

Thus, as shown above the emission factor is expressed in units of mass of species n emitted per unit mass of carbon burned. To convert this emission factor to the more commonly used grams n produced per kg dry matter burned, EF_n is multiplied by the mass fraction of carbon in the fuel (~50%). In Eq. (3.2) $<EF_n>$ needs to be a *mass* average over the entire life of the fire. However, emission factors are typically determined at instantaneous measurements. A carbon budget is formulated from specific samples as opposed to being constructed from a continuous measurement. Since flaming and smoldering combustion are the two distinct phases of combustion, Ward and Hardy (1991) suggested that $<EF_n>$ could be weighted by emission factors for these two distinct components (EF_{nf} and EF_{ns}, for flaming and smoldering combustion, respectively) by the fraction of biomass consumed by each process.

ACPD
5, 10455–10516, 2005

Estimates of the weighting fraction vary in the literature. For grass and shrub fires flaming combustion dominates and likely accounts for 80% of fuel consumption (Shea et al., 1996; Ward et al., 1996). For boreal, temperate, and tropical forest combustion smoldering combustion can occur for days and hence integrated over the course of a fire becomes dominant. For example, the data from Susott et al. (1996) suggest that 35% and 65% of fuel consumption in temperate forests occurs in the flaming and smoldering stage, respectively. Reid et al. (1998) found that regionally over the Amazon Basin, the atmospheric CO to CO_2 ratio was consistent with an equal partition flaming and smoldering combustion.

In an effort to simplify combustion to its most fundamental principles, most metrics applied to emissions therefore involve the fractional rate of complete combustion. The most commonly used is *combustion efficiency*. Ward and Hardy (1991) defined the *combustion efficiency* (CE) as the ratio of carbon (C) emitted as CO_2 to the total amount of carbon emitted:

$$CE \equiv \frac{[C]_{CO_2}}{[C]_{CO_2} + [C]_{CO} + [C]_{CH_4} + [C]_{NMHC} + [C]_{PC}} \quad (3)$$

where the subscript CO is for carbon monoxide, CH_4 is for methane, NMHC is for non-methane hydrocarbons, and PC the particulate carbon emitted. Thus, by definition the combustion efficiency is the fraction of fuel carbon *emitted* by the fire that is completely oxidized to CO_2. Since environmental variables such as fuel size and moisture, wind speed, atmospheric relative humidity, and fire direction have measurable impacts on fire properties and hence the efficiency in which fuel burns, they are often manifest in a change in the combustion efficiency (Ward, 1991; Cachier et al., 1991). In general, when the CE exceeds ~90% a fire is typically in the flaming phase (Ward and Hardy, 1991) and combustion temperatures are high enough such that flames are clearly visible around the fuel. When CE is less than ~85% combustion is in the smoldering phase. The smoke emitted from most fires is a product of both flaming and smoldering combustion on different pieces of fuel, and can be considered as "mixed" phase.

ACPD
5, 10455–10516, 2005

Although the combustion efficiency is a useful quantity for fire models, it is difficult to adequately measure all individual contributions to the emitted carbon. To simplify matters we can use the fact that >90% of the carbon combusted in a fire is emitted in the form of CO_2 and CO, and <10% of carbon is in species such as hydrocarbons and particulate carbon. With this in mind, Eq. (3.3) is often simplified to the "modified" combustion efficiency, or MCE (Ward and Hao, 1992):

$$\mathrm{MCE} \equiv \frac{[\mathrm{C}]_{\mathrm{CO_2}}}{[\mathrm{C}]_{\mathrm{CO_2}} + [\mathrm{C}]_{\mathrm{CO}}} \tag{4}$$

Since hydrocarbon and particulate carbon are emitted in relatively small quantities relative to CO_2 and CO, the difference between CE and MCE is typically only a few percent. Ward and Hao (1992) found that typically the MCE can be related to the CE through the experimental empirical relation:

$$\mathrm{CE}=1.18(\mathrm{MCE})-0.18 \quad (r^2=0.99) \tag{5}$$

For *cerrado* (scrub forest), grassland, and tropical forest emissions in Brazil, Ferek et al. (1998) found a similar relationship:

$$\mathrm{CE}=1.22(\mathrm{MCE})-0.22 \quad (r^2=0.99) \tag{6}$$

MCE can also be related to the commonly used $(CO)/(CO_2)$ ratio

$$\frac{[\mathrm{CO}]}{[\mathrm{CO_2}]}=\frac{1-\mathrm{MCE}}{\mathrm{MCE}} \tag{7}$$

The most commonly reported value that is readily measured in most studies is the *emission ratio, ER,* of a trace gas that is typically normalised to a reference compound such as CO or more often CO_2. The emission ratio of a compound X normalised to CO_2, for example, is then given by

$$ER = \frac{\Delta[X]}{\Delta[\mathrm{CO_2}]} = \frac{[X]_{\mathrm{Plume}} - [X]_{\mathrm{Background}}}{[\mathrm{CO_2}]_{\mathrm{Plume}} - [\mathrm{CO_2}]_{\mathrm{Background}}} \tag{8}$$

ACPD
5, 10455–10516, 2005

where $[\,]_{Plume}$ is the measured concentration in the plume and $[\,]_{Background}$ the measured background concentration of the corresponding compound.

4. Source categories

4.1. Open fires

Various studies have been published dealing with the amount of biomass burned from various sources mainly in tropical regions (Seiler and Crutzen, 1980; Hao and Liu, 1994; Crutzen and Andreae, 1990; Andreae, 1991). The sources were identified to be mainly deforestation, shifting cultivation, savanna fires, fuel wood and the burning of agricultural residues. Most of these data were derived from extrapolations of local and regional observations and partly from satellite data, and typically ranges were given for each source. These sometimes differed by a factor of 4 between the lowest and the highest estimated value.

Andreae et al. (1991) estimate that 8700 Tg of dry matter are burnt annually. Sixty-six percent of the biomass is burnt in savanna and agricultural fires, while biofuel and tropical forests contribute about 15% to the total biomass burnt globally. The contribution of boreal forests is low compared to other areas. However, according to Levine (1996a) the biomass burned in boreal forests increased by a factor of 10 between the mid 1970's and the mid 1990's. Concerning the geographical distribution of the number of fire events, Africa is dominating with about 40% of all fires, about 25% occur in South America and about 35% are distributed over the rest of the world.

Savanna fires are the single largest category of biomass burning emissions worldwide (Crutzen and Andreae, 1990; Andreae, 1991, 1993; Hao and Liu, 1994). The reason for the high incidence of savanna fires is the seasonal cycle of wet season, during which biomass is produced, and the dry season, during which the biomass is turned into highly flammable material. Although in most cases fires are human induced, also natural induced savanna fires are common, when lightning strikes the dry vegetation.

ACPD
5, 10455–10516, 2005

In spite of the obvious importance of emissions from savanna fires to the troposphere there are still only a relatively small number of studies that have investigated the emissions from savanna fires.

Africa contains about two thirds of the world's savanna regions, and African savanna fires alone account for 30% of the biomass burning emissions in the tropics worldwide (Hao and Liu, 1994). Ninety percent of African savanna fires are believed to be human induced. Agricultural and pastoral practices include an annual burning of savanna vegetation. The reasons are clearing of dead or unwanted vegetation, fertilization, hunting practices, improvement of access for collection of food and other vegetation products (Andreae et al., 1996). Estimates of the impact of these practices vary by a factor of two. For example, Andreae et al. (1993) estimate that 820 million ha is burned in savannas annually, resulting in the combustion of about 3400–3700 Tg dry matter of biomass per year. Hao et al. (1996) estimated that the biomass burned in Africa is about 2000 Tg dry matter annually, and the area exposed to fires in African savannas covers about 440 million ha.

Hao and Liu (1994) published a comprehensive database for the spatial and temporal distribution of the amount of biomass burned in tropical America, Africa and Asia during the 1970s with a resolution of $5^{\circ}\times5^{\circ}$. Recently, a number of papers make use of new satellite products to derive an overview of the spatial and temporal distribution as well as the interannual variability of biomass burning emissions using remotely sensed observation of fire counts with a resolution up to $1^{\circ}\times1^{\circ}$ (Duncan et al., 2003; Ito and Penner, 2004; Hoelzemann et al., 2004; van der Werf, 2004). The maximum amounts of biomass burning occur between February and April in the Northern Hemisphere and between August and October in the Southern Hemisphere. As the major burning areas they identified Southeast Asia, Africa, Brazil, Indonesia and Malaysia.

4.2. Domestic fires

Little is known about the contribution of domestic fires to global biomass-burning emissions. There are a few studies on emissions of trace gases from domestic fires (Bro-

ACPD
5, 10455–10516, 2005

card et al., 1996; Brocard and Lacaux, 1998; Czapiewski, 1999; Bertschi et al., 2003). Based on data of the 1980's, 15% of the global energy requirements are met by the burning of biofuel (Hall, 1991). Recent studies by the Food and Agricultural Organization of the United Nations even estimate that up to 25% of the global energy requirements is produced using biofuel. Seventy five percent of the world's population use wood as the main source of energy (Marufu et al., 1997). In Africa, the use of fuel wood and charcoal supplies 90% of the energy in private households and 60% of the total energy consumption (Brocard and Lacaux, 1998). As reported by Andreae (1991), the per capita consumption of fuel wood in Africa is about 475 kg per year. Recent estimates showed that this value may be significantly underestimated since official statistics only account for sales data of fuel wood and do not consider collected bio fuel. Marufu et al. (1997) reported a typical annual consumption of fuel wood of the order of 950 kg per capita and a consumption of agricultural waste of the order of 130 kg per capita for rural areas in Zimbabwe. Kituyi et al. (2001a, b) report similar results for Kenya. The use of agricultural waste, which is available only for a few months per year, adds up to 270 kg per capita and year. With increasing population in Africa and also other third world countries the consumption of bio fuel will increase considerably. This may have, on the other hand, an impact on the availability of biofuel in wildfires. Furthermore, in the next decades the change of climate may lead to a considerable change in land use. Due to the burning of forests to gain farmland, changes in urbanisation structures, the increasing burning of agricultural waste, and the use of biomass as energy source frequent biomass burning events may occur in areas where presently no or low amounts of biomass burning are observed. As a consequence, a change in the combustion characteristics can be expected in the future. The impact of these changes on tropospheric chemistry and climate can hardly be estimated today.

ACPD
5, 10455–10516, 2005

5. Gaseous emission products

The first investigations on biomass-burning emissions started with studies of emissions from the burning of refuse, waste, slash, and other organic material (Darley et al., 1966; Gerstle and Kemnitz, 1967; Boubel et al., 1969; Sandberg et al., 1975; Wong, 1978). The first published studies investigating emissions from open savanna fires were made in South America by Crutzen et al. (1985) in the Brasilian Cerrado. Detailed investigations in this area were further made during the BASE-A and BASE-B experiments in Brazil (Ward et al., 1992). In the last years some studies were conducted in Australia, where savanna fires occur every year in the northern tropical regions (Ayers and Gillet, 1988; Hurst et al., 1994a, b). The first published measurements on biomass-burning emissions in Africa were made in West Africa by Delmas (1982). They studied the regional atmospheric chemistry over the Congo forest. A number of following studies indicated that biomass burning in sub-Sahelian savannas have far-reaching impact on the atmospheric environment (Cachier et al., 1991; Andreae et al., 1991; Bingemer et al., 1992; Cros et al., 1991; Helas et al., 1995b; Lacaux et al., 1992). Later a number of large integrated studies followed in Central and Southern Africa such as FOS/DECAFE (Lacaux et al., 1995), TRACE-A (Andreae et al., 1996), SAFARI-92 (Andreae et al., 1996; Lindsay et al., 1996), SA'ARI (Helas et al., 1995b), SAFARI 2000 (Swap et al., 2003) (see Table 1 for an overview).

Compared to savanna and rain forests, gaseous emissions from boreal and temperate forest are clearly more underrepresented in the literature. While CO_2 and CO are commonly measured and reported, there are few reports of VOCs and oxygenates from open burning for these fuel types. This is particularly troublesome as we know that at least particle emissions for such fires differ from other fuel sources (Reid et al., 2005a, b). It is essential to know if the VOC/CO ratios commonly applied from other fuel types are at all close to reality.

In the following sub-sections emissions of carbon monoxide, methane, nonmethane hydrocarbons, oxygenated hydrocarbons, halogenated hydrocarbons, and nitrogen

ACPD
5, 10455–10516, 2005

containing compounds are discussed. The main focus is laid on *emission ratios*, in most cases relative to CO_2, a value that relatively easy to determine from the measurement of trace gas concentrations inside and outside of biomass burning plumes. Most studies investigating reactive trace gas emissions form biomass burning also measure the excess mixing ratio of CO_2. Emission ratios are therefore available for most field and laboratory studies, at least for selected trace compounds. A more important parameter in the sense of an assessment of the impact of biomass burning emissions and a potential up-scaling to a regional or global scale is the *emission factor*. Full fire lifecycle emissions factors are seldom directly measured since except for laboratory studies under controlled conditions the fuel load and composition are not known. Sometimes, such values are reported without having the appropriate information (see below) and based on rather crude assumptions. If ever, these data have to be used with great care, since the uncertainties are huge and sometimes not even known.

5.1. Carbon monoxide

Following carbon dioxide, which is the main compound emitted from any combustion process of organic material, carbon monoxide is the second most important compound. With a few exceptions most gaseous trace compounds are emitted during the smoldering stage of a fire and are well correlated to CO. Therefore, excess CO is often used to normalize emission ratios of these compounds.

Typical molar emission ratios ($\Delta(CO)/\Delta(CO_2)$) observed for different biomass burning events in various ecosystems range from lowest values of about 2% to highest values of about 20% depending on the biofuel and the phase of the fire (Greenberg et al., 1984; Crutzen et al., 1985; Andreae et al., 1988; Bonsang et al., 1991, 1994; Griffith et al., 1996; Kaufman et al., 1992; Ward et al., 1992; Hurst et al., 1993; Ferek et al., 1998). Savanna fires are typically a flaming front moving across the landscape leaving a large area of smoldering material. What is typically observed are therefore emissions from a mix of different phases of the fire. During the FOS/DEFACE experiment in the Ivory Coast Bonsang et al. (1995) report molar emission ratios $\Delta(CO)/\Delta(CO_2)$ ranging

from 6 to 15%. Similar observations were made during SAFARI 92 in southern Africa, where ratios between 4.4% and 9.4% were found for different types of fires (Koppmann et al., 1997). Compared to that, the ratios observed in boreal forest fires were often at the upper end of the ranges observed for savanna fires. For example, during International Crown Fire Modeling Experiment (ICFME) study conducted in a jack pine (*Pinus banksiana*) stand in the North West Territories, Canada, Cofer et al. (1998) observed similar emissions ratios of CO relative to CO_2 between 9.4 and 11.3%. These data are consistent with the results of various laboratory studies. In experiments burning different bio fuels under controlled conditions, values between 1.3% and 25% are reported (Darley et al., 1966; Boubel et al., 1969; Talbot et al., 1988; Lobert et al., 1989; Czapiewski, 1999). In a detailed study Lobert (1989) reported emission ratios varied between 4% and 10%. Czapiewski (1999) gave average emission ratios of 10.7% for the burning of different typical fuel woods in laboratory studies and 7.1% for the measurements at domestic fires using fuel wood of the same species. Similar values were founr by Brocard et al. (1996) for domestic fires in West Africa. Table 2 summarizes the published emission ratios.

In a few studies *emission factors* of CO from various types of fires have been determined. Hegg et al. (1990) and Laursen et al. (1992) report values between 34 and 175 g/kg (g compound per kg dry weight of matter burned) for different fires in North America with an average of 95±16 g/kg. Looking into these data in detail shows, that Laursen et al. (1992) report emission factors for the same fires as do Hegg et al. (1990), but report different emission factors, without giving any comment on these differences. Laursen et al. (1992) added the results of the investigation of six more fires increasing the number of investigated fires from seven to thirteen. They came up with the same average emission factors within their standard deviations, the values of which have been mentioned above. Hobbs et al. (1996) report similar values between 88 and 168 g/kg for prescribed fires in the Pacific Northwest. CO emission factors for grassland and forest fires are in the range of 56–120 g/kg (Ferek et al., 1998). There is also little information about emission factors for domestic fires, ranging from 30 g/kg

ACPD
5, 10455–10516, 2005

for open domestic fires (Brocard et al., 1996) and up to 170 g/kg for fires in cook stoves (Zhang et al., 1999). In summary, CO emission factors vary at least a factor of two for different types of fires.

Due to the rather long lifetime of CO in the troposphere, CO from biomass burning can be distributed over a wide area and can be used as a tracer of biomass burning plumes in the remote troposphere. McMillan et al. (2003) reported remotely sensed column densities of CO obtained during SAFARI 2000 of $1.5{\cdot}10^{19}$ cm^{-2} over a smoke plume in South Africa which was about an order of magnitude higher than the column density in clean air in the same region. Matsueda et al. (1999) attributed their observations of events of high CO mixing ratios in the southern subtropical upper troposphere to transport processes from biomass burning in south east Asia to the western South Pacific.

Duncan et al. (2003) derived global CO emissions from biomass burning using remote sensed observations of fire counts. They gave global CO emission rates of 511 Tg for 1997 and 565 Tg for 1998, and a significantly lower value of 429 Tg for 1999. Recently, van der Werf et al. (2004) used several satallite products to derive global biomass-burning emission rates from observed monthly anomalies of atmospheric CO. Applying a forward biogeochemical model they came up with a global emission rate of $495{\pm}78$ Tg yr^{-1} for the period 1997–2001.

5.2. Methane

Methane is not a very reactive compound and thus does not play such a significant role in the chemistry of biomass-burning plumes as other volatile organic compounds. Nevertheless, methane is the second most important fuel for tropospheric chemistry, and as a strong infrared absorber and important greenhouse gas, contributes significantly to the stratospheric water vapor budget and directly affects stratospheric ozone chemistry. Biomass burning is the third largest source for CH_4, contributing about 40 Tg/year to the global methane emission rate (IPCC, 2001).

The molar emission ratio relative to CO ($\Delta CH_4/\Delta CO$) reported for various biomass-

ACPD
5, 10455–10516, 2005

burning events range from about 1% to up to 17% (Hegg et al., 1980; Kaufman et al., 1982; Ward et al., 1982; Hurst et al., 1994). The molar emission ratios relative to CO_2 ($\Delta CH4/\Delta CO_2$) range typically from 0.1% to 2% (Greeberg et al., 1984; Crutzen et al., 1985; Bonsang et al., 1991; Cofer et al., 1990; Griffith et al., 1992; Kaufman et al., 1992; Ward et al., 1992; Hurst et al., 1994)

Bonsang et al. (1995) reported molar emission ratios of CH_4 relative to CO_2 for savanna fires investigated during the FOS/DEFACE experiment in the Ivory Coast. The molar ratios varied between 0.32 and 0.46% for fires with high combustion efficiency. For fires with low combustion efficiency they report a twice as high ratio of 0.78%. Koppmann et al. (1997) report very similar ratios of 0.26 and 0.28% for mainly flaming fires. In the plume of a wildfire this ratio increased to 1%. Alvala and Kirchhoff (1998) report average CH_4 mixing ratios observed during the SCAR-B experiment in August 1995 in the Brasilian cerrado of 1739±20 ppb. This value is well above the average mixing ratio of 1690±26 ppb derived from the NOAA CMDL curve for that region and indicates a significant contribution of biomass burning to the CH_4 mixing ratios at the time of measurement. Ferek et al. (1998) report a emission ratio of $\Delta CH_4/\Delta CO$ of 0.098±0.01 for fresh smoke measured in the same experiment. This value is similar to ratios reported for the BFA study (0.107±0.004, Blake et al., 1997) and TRACE A (0.094±0.013, Blake et al., 1996a). Cofer et al. (1998) reported emission ratios between 0.4 and 1.4% for crown fires during the International Crown Fire Modeling Experiment (ICFME) conducted in the North West Territories, Canada. The published data are summarized in Table 3.

Although for methane it is even more important to know the emission factors for an up-scaling to global emission rate than for CO, methane emission factors reported from the few studies available vary by a factor of 20 and range between 1 and 20 g/kg (Hegg et al., 1990; Laursen et al., 1992; Hobbs et al., 1996; Ferek et al., 1998). The average emission factor can be fixed at about 3 and 10 g/kg and for flaming and smoldering combustion, respectively. However, the overall variation in these figures is at least on the order of ±70%.

ACPD
5, 10455–10516, 2005

Methane mixing ratios increase globally with the rate of increase showing significant year-to-year variations (cf. Dlugokencky et al., 2001). Lowe et al. (1994) reported the ^{13}C record of atmospheric methane and showed that there is evidence for these variations being caused by changing sources. At least part of the variations is attributed to a year-to-year variation of biomass burning events. Due to its long tropospheric residence time global variations in biomass burning events have a direct impact on the global CH_4 balance.

5.3. Nonmethane hydrocarbons

In addition to CO_2, CO and CH_4 hundreds or even thousands of volatile organic compounds are emitted from biomass burning. The identification of the various compounds increased considerably with the improvement of analytical techniques in the last 20 years. A comprehensive compilation of VOC species emitted from biomass burning can be found in papers such as Blake et al. (1996b), Koppmann et al. (1997), Ferek et al. (1998), and Ciciolli et al. (2001). Most of the early studies on hydrocarbon emissions from biomass burning dealt with light hydrocarbons in the C_2-C_3 range (Crutzen et al., 1979, 1985). Greenberg et al. (1984) reported results of field measurements of hydrocarbon emissions in the Cerrado (grasslands) and Selva (tropical forest) regions of Brazil in 1979 and 1980. They extended the range of investigated hydrocarbons up to C_{12} compounds. However, their hydrocarbon emission ratios were based on gas chromotography/flame ionized detection (GC-FID) analyses of canister samples and calibrated with a one-component standard based on neohexane, that may possibly lead to an underestimation of higher molecular weight compounds. They report $\Delta CO/\Delta CO_2$, $\Delta CH_4/\Delta CO_2$ and $\Delta NMHC/\Delta CO_2$ for Cerrado fires of 11.3 (range: 4.8–26.8)%, 0.6 (range: 0.2–2.4)% and 1.1 (range: 0.3–3.4)% mol C/mol, respectively. For the Selva fires they reported somewhat higher values of 11.9 (range: 4.7–30.2)%, 1.1 (range: 0.5–2.3)% and 1.2 (range: 0.4–2.8)% mol C/mol, respectively.

In the 1980s and 1990s a growing number of studies were published that deal with field measurements of emissions from biomass burning, especially in Africa (Delmas,

ACPD
5, 10455–10516, 2005

1982; Bonsang et al., 1991; Rudolph et al., 1995; Lacaux et al., 1995; Koppmann et al., 1997; Andreae et al., 1997). Bonsang et al. (1991, 1995) investigated hydrocarbons up to C_6 compounds, including reactive hydrocarbons such as isoprene and other dienes. They investigated savanna burning in West Africa at the Lamto reserve, Ivory Coast, located at the border of the tropical rainforest and the savanna. They reported hydrocarbon mixing ratios in the plume samples reaching ppm levels and thus exceeding mixing ratios representing background levels by orders of magnitude. Based on their measurements they derived an average molar emission ratio for $\Delta CO/\Delta CO_2$ of (11.04±4.39)% indicating that smoldering combustion dominated the fires they encountered during their measurements. The molar emission ratio of the sum of NMHC relative to CO_2 ($\Delta\Sigma NMHC/\Delta CO_2$) was found to be (0.81±0.38)%. The most abundant hydrocarbon emitted was ethene contributing 44% to the total measured NMHC emissions. Bonsang et al. (1991) stated that the NMHC all together represent a higher contribution than methane.

Koppmann et al. (1997) reported organic trace gas measurements made during SAFARI-92 in southern Africa. They found several hundred higher molecular weight organic compounds in plume samples of different types of fires, more than 70 of which could be identified. These compounds included alcohols, aldehydes, ketones, carboxylic acids, esters, ethers and furanes. They distinguished between different types of fires, an occasional wildfire, prescribed fires in the Kruger National Park and sugar cane fires. For enabling comparison with other data sets the emission ratio of the VOC versus CO_2 was separated for the emission ratio of the sum of C_2-C_4 hydrocarbons as well as the sum of organic trace gases with 5 or more carbon atoms. It can be seen that the emissions of the sum of the light NMHC are comparable or even larger than the emission ratio of methane. Their results showed further that the emission ratio of organic compounds with a carbon numbers of 5 or more add up to at least half of the contribution of light NMHC.

The molar emission ratios of the total measured organic compounds relative to CO_2 varied between $(13.7\pm0.9)\cdot10^{-3}$ for the wildfire and $(3.9\pm2.9)\cdot10^{-3}$ for the flaming sugar

ACPD
5, 10455–10516, 2005

cane fires, respectively. These values were in agreement with measurements of fires under laboratory conditions as reported by Czapiewski (1995), who gave an average emission ratio of the sum of organic compounds $3{\cdot}10^{-3}$. Lobert et al. (1991) reported an average of $11.9{\cdot}10^{-3}$ based on 10 different experiments. The ratio found for the Kruger National Park fire agreed with the laboratory measurements while the ratio found for the wildfire exceeded the laboratory values. The emission ratios of the predominantly flaming sugar cane fires were considerably lower than the results of the laboratory studies. This may be due to the fact that large flaming combustion can not be simulated realistically in confined fires which are controlled by their artificial boundaries. Especially the response of fires to wind and the access to oxygen for combustion, which affects mainly the flaming phases differs significantly between free and confined fires (Albini, 1993).

Ferek et al. (1998) report emission ratios for a variety of NMHC relative to CO with an emission ratio of $\Delta\Sigma$NMHC (C<11)/ΔCO of 0.095±0.01. They report the light alkenes, ethene and propene, ethane and acetylene being the dominant compounds in the emitted NMHC. Cofer et al. (1998) observed emissions ratios of total NMHC relative to CO_2 between 0.6 and 1.4% for crown fires and 18.5 and 33.5% for slash fires in a boreal forest during the ICFME study.

For domestic fires Brocard et al. (1996) reported an emission ratio for ΣVOC/CO_2 of 0.57% without stating which VOC were investigated in their study. Czapiewski (1999) investigated VOC ($<C_{12}$) from domestic fires and reported an emission ratio for ΣVOC/CO_2 of 1.6%. The emission ratios of ΣVOC given by Smith et al. (1992) are not significantly different from those reported by Czapiewski (1999). Table 4 summarizes the published emission ratios.

As stated before the only way to estimate the total amount of a compound emitted per unit mass of fuel, a parameter that is actually needed for an up-scaling of biomass burning emissions, is the knowledge of the appropriate emission factors. In some studies emission factors were investigated and reported following the definition given above. But in most cases the fuel load and composition are not known. Nevertheless,

ACPD
5, 10455–10516, 2005

emission factors are reported.

For VOC only few investigations on *emission factors* are available. (e.g. Hao and Ward, 1993; Hurst et al., 1994; Ferek et al., 1998; Sinha et al., 2003). Ferek et al. (1998) report emission factors of volatile organics ($<C_{11}$). They integrated all peaks and applied the methane mass response factor to calculate the total mass of carbon. Therefore, regrading the lower response of an FID for VOC with hetero-atoms or functional groups, these figures can be seen as lower limits of the emission factors. They reported 6–7 gC/kg for savanna and grassland fires, and 7 gC/kg and 17 gC/kg for the flaming and smoldering phase of forest fires, respectively. The variation in these figures was on the order of ±50%. Much lower values were reported by Sinha et al. (2003) for 10 fires inmvestigated during SAFARI 2000. They report a total VOC EF of about 2 gC/kg with individual EFs ranging from 1 to 10^{-3} gC/kg depending on the compound. Laursen et al. (1992) report an average emission factor of 1.78±0.33 gC/kg for North American fires, summing up only C_2-C_4 hydrocarbons. Borcard et al. (1996) report emission factors of 2.5±1.3 gC/kg for domestic fires without specifying the VOC taken into account.

At this point it is worthwhile to discuss the way emission factors are reported in the literature. A number of publications report emission factors, although they have not been directly measured. A compilation of emission factors for a large number of individual VOC for different types of biomass burning is given by Andreae and Merlet (2001).

However, most of these data are not original data but were calculated back from molar emission ratios after

$$EF_x = ER_{x/y} \frac{MW_x}{MW_y} EF_y \tag{9}$$

where EF_x is the emission factor of compound x, $ER_{x/y}$ is the emission ratio of compound x relative to reference compound y, MW_x and MW_y are the molecular weights of the compound x and reference compound y, and EF_y is the emission factor of the reference compound. Since in most cases the original literature does not explicitly give

an emission factor of the reference compound they used average emission factors of the reference compound (usually CO_2, sometimes CO) for the "appropriate type of fire" without stating how they derived those data. If emission factors were reported relative to the amount of carbon burned, a "default carbon content" of the burnt matter of 45% was applied.

By applying this procedure a number of large errors, uncertainties in the coefficients and biases in the data propagate through the calculations. Robinson (1989) demonstrated in detail the difficulty to up-scale biomass burning emissions. This holds true also for parameters that are based on measurements that have errors on the order of ±50% or even more and poorly documented basic data that are often based on educated guesses, but a necessary input into those estimates. As an example, Ferek et al. (1998) could show that a relatively small variation in MCE of 10% leads to a variation in the EF of nonmethane hydrocarbons of a factor of three.

5.4. Oxygenated hydrocarbons

In addition to the nonmethane hydrocarbons, a large variety of organic compounds containing oxygen, nitrogen and sulfur or functional groups are emitted by biomass burning, mainly during the smoldering phase of fires. Among them, oxygenated compounds seem to be the most abundant. These compounds include alcohols, aldehydes, ketones, carboxylic acids and esters. Although a quantitative determination of oxygenated hydrocarbons is still a challenge, the increasing awareness that these compounds are important players in tropospheric chemistry has lead to significant ongoing research. A number of recent studies give evidence that biomass burning emissions may be the source of oxygenated organic compounds in remote areas and even in the free troposphere (Lefer et al., 1994; Singh et al., 1994; Talbot et al., 1999; Jacob et al., 2002). Further developments of sampling reactive compounds, gas chromatographic techniques and new techniques such as Proton Transfer Mass Spectrometry (PTMS) allows studies of biomass burning emissions to be extended to these compounds. A variety of oxygenated compounds have been detected in the smoke of biomass burning

ACPD
5, 10455–10516, 2005

emissions both in laboratory (Lipari, 1984; Czapiewski, 1999) and field studies (Atlas et al., 1996; Koppmann et al., 1997; Holzinger et al., 1999).

The abundance of oxygenated volatile organic compounds in biomass-burning plumes competed or even exceeded that of the hydrocarbons. Manø (priv. comm.) reported a molar emission ratio for the sum of identified oxygenated compounds relative to CO_2 from laboratory fires of 7.5×10^{-3}. Czapiewski (1999) reported from laboratory experiments and field measurements of domestic fires that aldehydes (formaldehyde and acetaldehyde not included), ketones and furanes make up 21% of the total emissions of organic compounds from fuel wood burning. Although she found no significant correlation of the contribution of oxygenated compounds to the total gaseous emissions her results indicate a slightly higher contribution of these compounds in fires with lower burning efficiency. She reported emission ratios of 3.5×10^{-3} (mol C/mol CO_2) for the field experiments and 3.7×10^{-3} (mol C/mol CO_2) for the laboratory measurements, which is about a factor of two lower than Manø's results.

In-situ techniques are also used to investigate biomass-burning emissions allowing the measurement of more reactive compounds at high time resolution and high accuracy. Hurst et al. (1994) used a FTIR technique to quantify emission ratios of formaldehyde and acetaldehyde from savanna fires in Australia. The found molar emission ratios of $\Delta HCHO/\Delta CO_2$ and $\Delta CH_3CHO/\Delta CO_2$ of $(0.21\pm0.14)\cdot10^{-3}$ and $(0.30\pm0.22)\cdot10^{-3}$, respectively. Holzinger et al. (1999) used a PTR-MS to measuring oxygenated compounds over Surinam, South America. They reported that the molar emission ratios relative to CO for formaldehyde and acetaldehyde ranged from 0.71 to 4.64% and 0.24–2.13%, respectively. Furthermore they were able to measure emission ratios of a number of other oxygenated compounds. They report molar emission ratios relative to CO for methanol (0.15–1.87%), and acetone (0.15–1.17%), as well as some other compounds such as acetonitrile (0.04–0.25%), and HCN (0.04–0.26%). Yokelson et al. (1999) and Goode et al. (2000) applied a FTIR in laboratory and field studies. They identified formic and acetic acid as well as a number of other oxygenated compounds such as methanol and hydoxyethanal.

ACPD
5, 10455–10516, 2005

Very recently, Trentmann et al. (2003) could show in a comparison of a model study with field measurements that neglecting the primary emissions of OVOC leads to unrealistically low ozone concentrations in young biomass burning plumes. This underlines the necessity to deepen our knowledge of OVOC emission behavior from biomass burning sources in order to correctly address their impact on regional and global ozone formation.

5.5. Halogenated hydrocarbons

Biomass burning is also a source of a variety of halogenated hydrocarbons. The emission of these compounds depends to a large extent to the chlorine content of the fuel material. Lobert et al. (1999) reviewed the literature and summarized the present state of knowledge concerning the chlorine content of various biomass fuels in different ecosystems. They gave best-estimate molar emission ratios (median values) relative to CO_2 for, CH_2Cl_2, CH_3CCl_3, and $CHCl_3$ of $65.8 \cdot 10^{-6}$, $3.45 \cdot 10^{-6}$, $0.43 \cdot 10^{-6}$, and $0.077 \cdot 10^{-6}$, respectively. Owing to the fact that methyl chloride is the most abundant halogenated hydrocarbon emitted from biomass burning, most studies deal with methyl chloride. Crutzen et al. (1979) reported field measurements of methyl chloride emissions, and gave an average molar emission ratio of $\Delta CH_3Cl/\Delta CO_2$ of $2.2 \cdot 10^{-5}$ with a range from 0.44 to $5.7 \cdot 10^{-5}$. Rasmussen et al. (1980) made laboratory experiments of methyl chloride emissions from smoldering combustion of different types of biomass. They reported emission ratios for methyl chloride relative to CO_2 ranging between $2.4 \cdot 10^{-5}$ and $30 \cdot 10^{-5}$ mol/mol. Similar values were also obtained by Lobert et al. (1991) in a laboratory study. They reported emission ratios versus CO between 1.8 and $44 \cdot 10^{-4}$ with an average of $16 \cdot 10^{-4}$. Based on their average of $73 \cdot 10^{-3}$ mol/mol $\Delta CO/\Delta CO_2$ this corresponds to an emission ratio versus CO_2 of $1.3 \cdot 10^{-5}$ and $32 \cdot 10^{-5}$ mol/mol with an average of $12 \cdot 10^{-5}$ mol/mol. Rudolph et al. (1995) reported emission ratios of $\Delta CH_3Cl/\Delta CO_2$ of $(4.30 \pm 0.95) \cdot 10^{-5}$ for biomass burning in equatorial Africa. Ferek et al. (1998) report $\Delta CH_3Cl/\Delta CO$ of $(5.2 \pm 1.7) \cdot 10^{-4}$ mol/mol for fresh

ACPD
5, 10455–10516, 2005

plumes observed in the SCAR-B experiment. This is comparable to emission ratios reported for BFA (Blake et al., 1997) and TRACE A (Blake et al., 1996) of $(3.1\pm0.3)\cdot10^{-4}$ and $(8.5\pm0.6)\cdot10^{-4}$, respectively. A compilation of molar emission ratios of CH_3Cl relative to CO_2 and CO is given by Lobert et al. (1999) for different types of ecosystems and fuels.

There are a few studies of biomass burning of halogenated hydrocarbons other than methyl chloride. Hegg et al. (1990) reported emission ratios for CF_2Cl_2. The average emission factor was 11±7 mg/kg biomass burned with a range of 0.4–45 mg/kg. Based on their emission factor of 1642 g of CO_2 per kg of biomass burnt Rudolph et al. (1995) calculated an upper limit of the molar emission ratio of $(2.4\pm1.5)\circ10^{-6}$ and a range of 9×10^{-8}–$1\cdot10^{-5}$.

Molar emission ratios of methyl halides (CH_3Cl, CH_3Br, and CH_3I) were reported by Andreae et al. (1996) determined during SAFARI-92 for different types of fires. Their molar emission ratios for CH_3Cl, CH_3Br and CH_3I versus CO_2 were $20\cdot10^{-6}$, $0.11\cdot10^{-6}$ and $0.09\cdot10^{-6}$, respectively. The corresponding values of the emission rates versus CO were $950\cdot10^{-6}$, $8.3\cdot10^{-6}$ and $2.6\cdot10^{-6}$, respectively. Ferek et al. (1998) found somewhat higher emission ratios for CH_3Br and CH_3I relative to CO observed in fresh biomass burning plumes during SCAR B of $(1\pm0.3)\cdot10^{-5}$ and $(5\pm2)\cdot10^{-6}$, respectively.

Rudolph et al. (2000) reported average emission ratios of methyl chloroform for different stages of laboratory fires (flaming, smoldering, complete fire). They found a high variability for different burning stages, but no statistically significant difference between flaming and smoldering stage and high or low chlorine content of the fuel. They derived average molar emission ratios of $(14.3\pm3.8)\cdot10^{-7}$ for $\Delta CH_3CCl_3/\Delta CO$ and $(17.6\pm4.5)\cdot10^{-8}$ for $\Delta CH_3CCl_3/\Delta CO_2$ for fires with an average $\Delta CO/\Delta CO_2$ ratio of (13.4±2.5)%. These values were considerably lower than previously reported upper limits of $(71.5\pm45)\cdot10^{-7}$ and $(43.1\pm19)\cdot10^{-8}$ (Rudolph et al., 1995). The published molar emission rates are compiled in Table 5.

With the phase-out of industrial production, the atmospheric burden of a number of halocarbons is rapidly declining. Therefore, for some halocarbons the potential impor-

ACPD
5, 10455–10516, 2005

tance of other than industrial sources is increasing. Rudolph et al. (2000) estimated under the assumption of a 100% effective phase-out of industrial methyl chloroform emissions the atmospheric methyl chloroform budget may be dominated by biomass burning emissions by 2025.

5.6. Nitrogen containing compounds

Besides carbon dioxide, carbon monoxide, methane, and volatile organic compounds biomass burning is an important source of reactive nitrogen compounds, which also have a significant impact on atmospheric chemistry. $\Delta NO_x/\Delta CO_2$ is reported to range between 0.5 and 3.5% mola/mol (Crutzen et al., 1985; Hao et al., 1987; Andreae et al., 1988; Griffith et al., 1991; Hurst et al., 1994). Delmas et al. (1995) reported measurements of nitrogen compounds during FOS/DECAFE. For nitrogen oxide emissions they reported average emission ratios $\Delta NO_x/\Delta CO_2$ (for both flaming and smoldering fires) on a mol/mol basis to be 0.14 (0.8–2.3)%. They found a good correlation between NO_x and CO_2 with correlation coefficients ranging between 0.76 and 0.93 indicating that both compounds are mainly emitted during the flaming phase of the fires. They showed only small differences between heading fires and backing fires. The emission ratio of total nitrogen oxides, $\Delta NO_y/\Delta CO_2$, proved to be only slightly larger than that of NO_x, namely 0.19 (0.17–0.21)%, indicating that most of these compounds are emitted as NO and NO_2. The emission ratio of ammonia, $\Delta NH_3/\Delta CO2$, was quite low, 0.057 $(0.023–0.10)\cdot10^{-3}$, but with a high variability. Most of the emission of ammonia occurs during the smoldering phase, the emission ratio being 20 times higher than during the flaming phase. The average emission ratio of $\Delta N_2O/\Delta CO_2$ derived from 15 smoke samples was 0.145 $(0.051–0.403)\cdot10^{-3}$.

Cofer et al. (1996) reported N_2O emission ratios relative to CO_2 for savanna fires investigated during SAFARI-92. They gave emission ratios of $(0.07\pm0.02)\cdot10^{-3}$ mol/mol for the flaming phase and $(0.14\pm0.02)\cdot10^{-3}$ mol/mol for the smoldering phase. These values agree surprisingly well with the data published by Delmas et al. (1995) and

ACPD
5, 10455–10516, 2005

seem to be more or less typical for savanna fires. However, these emission ratios can obviously not extrapolated to biomass burning emissions in other regions of the world. For fires in the wetlands or boreal forests N_2O emission ratios are about a factor of 2 higher for flaming combustion and a factor of 3 higher for smoldering combustion. Cofer et al. (1989) reported N_2O emissions from the burning of chaparral in southern California and boreal fires in northern Ontario, Canada. They distinguished between flaming, smoldering and mixed combustion. For the California fires $\Delta N_2O/\Delta CO_2$ ranged between $(0.14\pm0.02)\cdot10^{-3}$ mol/mol and $(0.21\pm0.01)\cdot10^{-3}$ mol/mol for flaming and mixed combustion, respectively. For the boreal fires the emission ratios were on the same order of magnitude.

6. Isotopic composition of hydrocarbons from biomass burning emissions

Besides improved analytical techniques that allowed to considerably extend the spectrum of compounds measured in biomass burning plumes, new methods may give further insight into the impact of biomass burning emissions on the budget or trace gases in the troposphere. Among those are the measurements of stable isotope ratios ($\delta^{13}C$) in organic trace gases, recently reviewed by Goldstein and Shaw (2003).

A few measurements of stable carbon isotope ratios ($\delta^{13}C$) of VOC from biomass burning have been reported in the literature. The first measurements were carried out by Rudolph et al. (1997) on a C3 New Zealand Manuka plant. The values ranged from −31.4 to −23.7‰ with uncertainties ranging between 0.2 to 3.6‰. These values are very similar to carbon isotope ratio of the fuel wood with exception of large fractionations for 1-butene (−6.9±0.7‰) and ethyne (−13±1.6‰). Czapiewski et al. (2002) reported $\delta^{13}C$ values for 19 different VOC measured during the burning of Musasa and Eucalyptus wood in laboratory experiments. All values were within ±5‰ of the fuel wood $\delta^{13}C$ values. They took samples during the flaming and smoldering phases of the fires. The $\delta^{13}C$ values measured during the flaming phase was typically only 2.2±1‰ higher that those in the smoldering phase for any given compound. Increasing frac-

ACPD
5, 10455–10516, 2005

tionation was observed with increasing temperatures for most VOC. Two compounds differed from the general observations. Ethyne showed an enrichment of 25±5‰ relative to the burnt wood. A similar enrichment was observed for transportation related combustion processes by Rudolph et al. (1997). Czapiewski et al. (2002) suggest this to be an effect of recombination processes leading to the formation of ethyne during flaming combustion. CH_3Cl showed a significant depletion of about −25‰ relative to the burnt wood, but no difference in fractionation between the flaming and the smoldering phase. A similar effect was observed by Rudolph et al. (1997). The burning of Manuka resulted in a depletion of −17‰ compared to the burnt wood. Presently, there is no explanation for the depletion processes leading to the observed $\delta^{13}C$ values for CH_3Cl from biomass burning. O'Malley et al. (1997) reported $\delta^{13}C$ values for $>C_{11}$ aliphatic hydrocarbons from various bio fuels. Emissions from C3 plants were depleted by 7.5–11.5‰ while emissions from C4 plants were depleted by 3.9–5.5‰. Depletion increased with increasing carbon number.

The analysis of carbon (and in the near future also hydrogen) stable isotope ratios ($\delta^{13}C$ and δD) in organic trace gases in the troposphere may become a useful tool to address the impact of biomass burning emissions at various temporal and spatial scales.

7. Impact of VOC emissions on formation of ozone

At the same time studies on biomass burning in African savannas were carried out (see above), evidence grew that the fires may be the main cause for an enhancement of ozone on a regional and even a global scale. A large number of studies investigated the impact of biomass-burning emissions and the subsequent photochemical oxidation of the emitted trace compounds on the formation of ozone in different regions of the world, such as Africa (Cros et al., 1988; Marenco et al., 1990; Helas et al., 1995a; Chatfield et al., 1996; Thompson et al., 1996a, b, 1997; Marion et al., 2001), Asia (Chan et al., 2001; Thompson et al., 2001), North America (Anderson et al., 1994;

ACPD
5, 10455–10516, 2005

McKeen et al., 2002), and South America (Delany et al., 1985; Browell et al., 1996). Another effect of the impact of biomass burning plumes was the tropical ozone maximum spanning from Africa across the Atlantic to South America (Cros et al., 1988, 1991; Fishman et al., 1991; Andreae et al., 1994; Olson, 1996). Additionally, African fires were thought to be the source of considerable air pollution, even over the remote Atlantic Ocean. Koppmann et al. (1992) reported elevated mixing ratios of CO and a number of light hydrocarbons in the marine troposphere that they attributed to biomass burning emissions in Africa.

There are a number of studies modeling the ozone formation in fresh biomass burning plumes and the impact of the plume chemistry on the composition of the atmosphere. Mauzerall et al. (1998) modeled the formation of ozone in biomass burning plumes based on results of the TRACE-A campaign over the south Atlantic. The found the highest ozone formation rates in fresh plumes in low altitudes. An up-scaling of $\Delta O_3/\Delta CO$ in aged plumes based on CO emission rates gave an ozone formation rate of $17{\cdot}10^{10}$ molecules ozone cm^{-2} s^{-1}. This corresponds to a regional enhancement of the ozone column density of about 10 Dobson units based on an average plume lifetime of 2–3 weeks. The estimated photochemical formation rate of ozone in biomass burning plumes may explain an increase of tropospheric ozone over the tropical south Atlantic of up to 30%. Chandra et al. (2002) estimated a net increase of the tropospheric ozone column density of about 10% in the tropics due to biomass burning emissions.

A model analysis of data obtained during the PEM-Tropics A campaign, which took place during the burning season, was conducted by Schultz et al. (1999). The comparison of a global 3-D simulation with and without biomass burning emissions showed that biomass burning caused an increase in ozone mixing ratios over the tropical South Pacific of 7–8 ppb at all altitudes.

From a 3-D global chemical transport model Galanter et al. (2000) estimate that biomass burning emissions contribute indirectly about 50% of the ozone concentrations observed over major tropical burning regions. This is in agreement with calculations

reported by Bonsang et al. (1994) based on measurement during the FOS/DECAFE experiment in western Africa. Helas et al. (1995a) conclude from measurements of ozone mixing ratios in photo smog layers over western Africa that source of ozone formed photochemically from biomass burning emissions is similar in strength to the input from the stratosphere into the troposphere.

In order to estimate the impact of VOC on the formation of ozone in the early stage of biomass burning plumes, Poppe et al. (1998) conducted simple model calculations using the Regional Acid Deposition Model (RADM2) published by Stockwell et al. (1990). The calculations were initialized for case studies with measured mixing ratios obtained during SAFARI-92. The model calculations showed that ozone mixing ratios reached a maximum mixing ratio of 134 ppb after 30 sunlit hours, if only CH_4 and CO as oxidizable carbon compounds are taken into account. Taking into account the measured VOC the ozone mixing ratio increases rapidly to values around 90 ppb within the first two hours after the emissions, followed by a further slower increase to about 195 ppb. Thus, the mixing ratio of ozone in the plume is about 45% larger if the impact of VOC is included with the peak mixing ratio reached about 30 h after the emission. These model results are consistent with observed increase of ozone mixing ratios in plumes of prescribed burns of conifer slash (Stith et al., 1981). They report ozone mixing ratios near the top of the plumes as high as 44 ppb above ambient values with an ozone formation even after plume travel time of more than 1 h.

Based on the global distribution of biomass burning events Marufu et al. (2000) estimated the impact of ozone formed in biomass burning plumes in the lower troposphere. They estimate that on a global scale about 30 Tg of ozone are formed annually due to biomass burning emissions of VOC. Emissions from Africa alone contribute about 35% to this value. A somewhat higher estimate is reported by Sanhueza et al. (1999) who investigated boundary layer ozone at a savanna site in the Orinoco basin. They extrapolated their results to a global scale and estimated an upper limit of ozone production from savanna fires of 67–120 Tg/year.

Based on the total mass of ozone formed in the troposphere (4580 Tg ozone/year)

ACPD
5, 10455–10516, 2005

and removed from the troposphere (4240 Tg ozone/year) (Ehhalt, 1999), the contribution by photochemical processing of biomass burning emissions does not play a significant role on a global scale. However, on a regional scale and during the biomass burning season ozone formation rates in biomass burning plumes may have a considerable impact on the local and regional air quality.

8. Extrapolations to global emissions

The typical samples of biomass burning emissions described above are not likely to be representative for biomass burning on a global scale, since they represent only a very limited fraction of the areas burnt globally each year. Therefore, any extrapolations of emission ratios to global scales are highly uncertain (see Robinson, 1979). Although we are aware of all these uncertainties, it is nevertheless worthwhile to compare the emissions of organic trace gases with global budgets at least to get an idea about the impact of biomass burning emissions to atmospheric chemistry. Table 7 summarizes the emission of total carbon species and CO from the various types of biomass burning based on compilation of literature data (Andreae, 1991, 1993; Hao and Liu, 1994; Andreae et al., 1997, and references therein). Despite the fact that VOC emission ratios are commonly reported relative to CO_2, the emissions of VOC are better correlated with CO than with CO_2. Therefore, extrapolations of global emissions are often based on VOC/CO emission ratios There are several estimates published in the literature, but all are based only on small data sets obtained in very limited areas. Bonsang et al. (1991) used the results obtained during FOS/DECAFE to estimate a global emission rate of VOC of $12{\cdot}10^{12}$ g C/year. One has to notice, however, that this estimate is based on measurements of light nonmethane hydrocarbons only. Lobert et al. (1991) estimate a global emission rates based on their laboratory studies of $42{\cdot}10^{12}$ g C/year. These values seem to be something like a lower and upper limit of global emission rates. Koppmann et al. (1997) report an estimate of total carbon released in form of VOC (CH_4 not included) based on their lower and upper limits of VOC/CO emission ratios

ACPD
5, 10455–10516, 2005

observed during SAFARI-92 between $25{\cdot}10^{12}$ g C/yr and $48{\cdot}10^{12}$ g C/yr.

Presently, the available data on sources of atmospheric CO are not sufficient to fully characterize the global distribution of CO in the atmosphere. Summarizing the investigations of CO emissions from biomass burning the global emission rate seems to be on the order of 500 Tg per year with a variation of −100/+250 Tg per year. Furthermore emission rates are highly variable. The total source strength of CO is estimated to be 2780 Tg yr^{-1} (IPCC, 2001). With respect to this figure, biomass-burning emissions contribute about 25% to the total source strength. However, taking into account that the global source strength given by IPCC (2001) includes the formation of CO from the oxidation of VOC, part of which are again due to biomass-burning emissions, fires contribute about 40% to the total source strength. This indicates that there is certainly a need to increase the database on emission rates of CO from biomass burning. First measurements using remote sensing from satellites have been done at least for short time periods (cf. Reichle et al., 1990), that clearly showed the impact of biomass burning on the global distribution of CO. Here, current and future satellite instruments may help to fill the gaps to understand the global budget of the most important trace gas fueling tropospheric chemistry.

Results from Measurement of the Pollution in the Troposphere (MOPITT) satellite sensor on Terra are only now beginning to appear in the literature. While several case studies have been performed (e.g., Bremer et al., 2004; Liu et al., 2005), the very first global analyses othat include biomass burning are very recent. Notably, Pétron et al. (2004) found that vegitation fires produce somewhat higher CO emissions than previous thought, on the order of 375–400 Tg CO/yr.

These emission rates are good examples for the problems arising from extrapolations of data obtained at a very limited location at a certain time in biomass burning season, not even knowing if all relevant organic emissions have been taken into account. The range of the global annual emission rates is at least a factor of three, and this may even be underestimated. Assuming the estimate of annual global anthropogenic VOC emissions of about 100 TgC is right, and assuming further that 90% of all biomass

ACPD
5, 10455–10516, 2005

burning events are human induced and thus contribute to the amount of anthropogenic emissions, the range of VOC emission rates from biomass burning between ~10 and ~50 TgC/yr leads to a contribution of biomass burning to the total anthropogenic VOC emissions between 10 and 40%. As discussed above these emissions have a significant impact on the global environment, through photochemistry, radical cycling, photo oxidant formation and the self cleaning capacity of the atmosphere. An assessment of the state of the atmosphere and propable future changes especially in the scope of global change can only be done by climate models implementing detailed information of the chemical processes in the atmosphere. These models need much more accurate emission inventories than those presently available. Since biomass burning emissions contribute significantly to the budget of reactive gases in the atmosphere the large uncertainties in the emission data are highly unsatisfactory.

9. Discussion, summary and recommendations for future work

In the last 30 years it has become clear that biomass burning is an important source of trace gases in the atmosphere. Understanding atmospheric chemistry on a regional and global scales and as well as the interdependence of chemical processes and climate change requires a reasonable knowledge of the temporal and spatial distribution of biomass burning emissions as well as the trace gas composition emitted from fires into the troposphere.

Presently, there is a debate about the trend in the global average OH radical concentration. It is not known if the self-cleaning capability of the atmosphere will increase or decrease in the future, nor is it known in which way climate change, which will be followed by a change in biosphere-atmosphere interactions, will affect tropospheric chemistry. The main impacts in this context are any changes in the sources and/or sinks of reactive trace gases which on the other hand is to a large extent influenced by any change in biomass burning emissions.

The most significant effect will occur in the tropics where anthropogenic emissions

ACPD
5, 10455–10516, 2005

from fossil fuel burning are relatively low. In these regions biomass burning plays and will play an important role in the trace gas cycles and thus in photochemical processes. To account for this impact, an "inventory" of biomass burning events together with suitable emission algorithms are needed assess the contribution of biomass burning to global change.

In this paper we gave an overview of gaseous emissions from biomass burning. Up to now, results have been reported from numerous field studies concerning emissions from open fires but also from domestic fires. The results show that besides the main products carbon dioxide, carbon monoxide and methane, a tremendous variety of organic compounds are emitted from biomass burning. The emission ratios of light non-methane hydrocarbons (C_2-C_4) relative to CO_2 typically range between 0.2 and about 1% and thus are on the same order of magnitude as the emission ratio of methane.

The emission ratios of higher molecular weight VOC (>C_5) relative to CO_2 (on a mol carbon to mol CO_2 basis) seem to be typically in a range of 0.1 to 0.5% depending on the phase of the fire. During the smoldering phase the emission ratio is found to be at the upper limit of this range. Although only a few data sets on these compounds are presently available, they seem to contribute much more to the overall VOC emissions than previously thought. This has significant implications for atmospheric photochemistry. The oxidation of these compounds, usually initiated by the reaction with OH radicals, leads to the formation of aldehydes and ketones. Deep convective clouds which are often observed in connection with huge biomass burning events may transport the plumes into the upper troposphere. In this critical region of the atmosphere photolysis of these compounds leads to the formation of HO_x radicals and considerably influences photochemistry in this region.

The most abundant halogenated hydrocarbon emitted from biomass burning is methyl chloride. Emissions from biomass burning contribute about 20% to the global budget of this compound. The emission rates of other halogenated compounds decrease with increasing carbon number. The only other halogenated compound emitted in significant amounts is dichloromethane. Here biomass burning contributes to about

ACPD
5, 10455–10516, 2005

12% of the global budget. For other halogenated compounds biomass burning emissions seem to be of minor importance.

A number of laboratory studies have shown important functional dependencies of trace gas emissions from burning conditions like mass of the burnt fuel, water content of the fuel, volume to surface ratios. The distribution of emissions in different compound classes as well as the emission ratios during different stages of the fire has been investigated. Of the organic compounds alkenes are the most abundant compounds emitted with a contribution of 25% to the total organic compounds. Alkanes follow with 17%, ketones with 11%, aromatics, furanes and alkynes with about 8% each. About 30% of the organic compounds are oxygenated compounds. Measurements of those compounds in biomass burning plumes are only sparsely reported in the literature.

Measuring stable isotope ratios in VOC will allow in the near future to attribute more precisely the contribution of biomass burning emissions to the organic trace gas budget of the troposphere and thus allow to estimate the impact of those emissions on the regional and global photo oxidant formation.

An important point that should not be left out in discussing VOC measurements as well as emission ratios and emission rates based on these data during the last two or three decades are experimental problems. Although having been considerably improved, measuring the concentration of VOC in the atmosphere is still a challenge and especially was in the past. Several intercomparison experiments showed that despite the fact that the precision of measurements was on the order of a few percent, the accuracy often was as low as 50% or less, and improved to 20–30% in the last ten years (Apel et al., 1994, 1999, 2003; Slemr et al., 2002). In addition, these intercomparisons covered only a limited set of mostly "well behaving" VOCs. Biomass-burning emissions contain hundreds and thousands of compounds only part of which are typically covered by the applied measuring methods. Thus, depending on the compound, already the "basic" input data may have large uncertainties. Concerning the measurements of other trace compounds such as nitrogen oxides or ozone one has to keep in mind that applying these methods to biomass burning emissions in an environment with a com-

ACPD

5, 10455–10516, 2005

plex chemical composition may lead to artifacts that may alter the "real" concentrations considerably due to instrumental interferences. Often, these experimental details are not discussed in the literature and appropriate tests of the instrumentation have not been carried out.

Another point is that measurements are seldom done in the immediate vicinity of a fire, but more often in the plumes at certain distances from the fire. VOC concentrations and patterns change with the age of a plume due to mixing with ambient air and photochemical processing especially of higher molecular weight or reactive VOC with short atmospheric lifetimes. This may lead to an underestimation of the "true" emission ratios and thus the emission rates.

Nevertheless, the increasing knowledge of the emission processes and the impact of the emitted compounds on atmospheric chemistry may be taken as the basis for further investigations of the complex interaction between biomass burning events and the atmosphere. By their circumstances, most of the in-situ investigations are only snapshots of the situation at a given time and a given place. Despite the large amount of data, we are far from having a detailed global picture of the distribution and amount of gaseous compounds emitted from biomass burning and their seasonal and year-to-year variations as well as any long term trends. Consistent long-term measurements are still missing as well as are measurements on a global scale.

Since it is impossible to do a field campaign in reaction to a sudden occurrence of a biomass burning event, the only chance to monitor the impact of such events are remote-sensing techniques, which could be improved considerably. With an increase in satellite capacity (e.g., MOPITT) of monitoring also trace gases in the troposphere it may be possible in the future to monitor also the temporal and spatial distribution of trace gas emissions from biomass burning at the best available resolution.

The growing number of investigations on biomass burning events in different ecosystems at different regions of the world has lead to a considerable increase in our knowledge of biomass burning emissions and their interactions with the atmosphere. Of course, the variability in the distribution and duration of biomass burning events is large

ACPD
5, 10455–10516, 2005

as is the emission of traces gases. Despite still existing uncertainties in the analysis of the contribution of biomass burning to the total emission of trace gases, the knowledge of emission ratios (the ratio of a trace gas emitted relative to CO or CO_2) as well as emission factors (the ratio of the mass of a trace gas emitted relative to the mass of the burnt fuel) has reached a level that is is possible at least for some specific compounds to use remotely sensed information to derive emissions from fire events with a relatively limited uncertainty .

As an example, the measurement of CO from satellites may lead to a global coverage of the effect of biomass burning emissions and together with emission ratios from field and laboratory studies may help to get also a global coverage of other trace compounds.

15 years ago, Robinson (1989) stated *"In sum, biomass burning, like many exchanges between the biosphere and the atmosphere is poorly mapped and varies tremendously, but systematically, in time and space. Past attempts to quantify biomass burning have employed ad hoc procedures and best available data. These have been unable to achieve any degree of precision"*. This review shows that the situation did improve, but the knowledge of the emission processes as well as the database covering the emission of important trace gases, although increasing, is still limited. At this point it is easy to say that more field and laboratory studies have to be done before the various puzzle pieces can be put together to form a clear picture of the interaction between biomass burning and atmospheric processes. Although this is a piece of research which is certainly necessary, the main step forward would be a better global coverage of some key compounds that allow to draw an estimate of the total trace gas emission from global biomass burning events.

ACPD
5, 10455–10516, 2005

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ACPD

5, 10455–10516, 2005

Table 1. Overview of large projects dealing with the investigation of biomass burning emissons.

Project	Acronym	Time of investigation	Area of investigation	Reference
Amazon Boundary Layer Experiment 2A	ABLE 2A	1985	Amazonia	Harriss et al., 1988
Amazon Boundary Layer Experiment 2B	ABLE 2B	1987	Amazonia	Harriss et al., 1990
Biomass Bunring airborne and spaceborne – Brazil A	BASE-A	September 1989	Brazilian grassland	Kaufman et al., 1992
Biomass Bunring airborne and spaceborne – Brazil B	BASE-B	August/September 1990	Brazilian grassland	Ward et al., 1992
Fire of Savannas/DECAFE	FOS/DECAFE	1991	West Africa	Lacaux et al., 1995
Transport and Chemistry near the Equator – Atlantic	TRACE-A	August–October 1992	South America and Southern Tropical Atlantic Ocean	Lindsay et al., 1996
Southern Africa Fire-Atmosphere Research Initiative	SAFARI-92	September–October 1992	Southern Africa	Andreae et al., 1996
Southern African Atmosphere Research Initiative	SA'ARI-94	1994	Southern Africa	Helas et al., 1995
Smoke, Clouds, and Radiation Brazil B	SCAR B	August/September 1995	Brazil	Kaufman et al., 1998
Experiment for Regional Sources and Sinks of Oxidants	EXPRESSO		Central Africa	
European Studies on Trace Gases and Atmospheric Chemistry	EUSTACH		Amazonia	Andreae et al., 2002
Fire Research Campaign Asia-North	FIRESCAN	1992–1993	Russia	FIRESCAN Science Team, 1994
Southern Africa Regional Science Initiative	SAFARI-2000	1999–2000	Southern Africa	Swap et al., 2003
International Crown Fire Modelling Experiment	ICFME		New Territories, Canada	Cofer et al., 1998

ACPD
5, 10455–10516, 2005

Table 2. Summary of published emission ratios $\Delta CO/\Delta CO_2$.

	Comments	$\Delta CO/\Delta CO_2$ %
Darley, 1966	Agricultural waste	5.4 (3–16)
Boubel, 1969	Stubble fields, Straw	6.6 (3–16)
Crutzen et al., 1979	Forest fires	12.4
		(11–14)
		19.9
		(16–25)
Greenberg et al., 1984	Cerrado (grassland),	11.9
	average range	4.7–30.2
	Selva (tropical forest),	11.3
	average range	4.8–26.8
Crutzen et al., 1985	Cerrado	11.6 (4.8–28)
Andreae et al., 1988		8.5 (5–8.8)
Cofer III et al., 1988	Chaparral	6.0
Lobert, 1989	Grass, straw, needles, laboratory study	7.1
Cofer et al., 1989	Forest fires	6.5 (5–8)
Cofer III et al., 1990	Boreal forests	6.6
Griffith et al., 1991		1.1–1.6
Ward et al., 1992	Boreal forests, flaming phase	6.7
	Smouldering phase	12.3
Kaufmann et al., 1992	Forests in Brasil (BASE-A)	5.4
Cofer III, 1993	Tropical fires	7
Hurst et al., 1994		5.8 (1.6–9.2)
Lacaux, 1995	Savanna, Westafrica, FOS/DECAFE	6.11
Bonsang et al., 1991, 1995	Savanna, Ivory Coast, January 1989, average	11.04±4.39
FOS/DECAFE	Flaming phase,	6.95±1.62
	Smoldering phase	15.42±1.91
Bonsang et al., 1995	Savanna, Ivory Coast, January 1991, average	11.44±8.00
FOS/DECAFE	Flaming phase,	5.44±1.63
	Smoldering phase	14.03±2.73
Hurst et al., 1996	Australian savanna	9.0
Andreae et al., 1996	Savanna South Africa, SAFARI	6.2
SAFARI	(mean of all savanna fires)	
Koppmann et al., 1997	wild fire, mainly wood	9.36±1.30
SAFARI		
Koppmann et al., 1997	Kruger National Park, SAFARI-92	5.29±0.71
Koppmann et al., 1997	Sugar cane fire #1, SAFARI-92	4.38±2.09
	Sugar cane fire #2, SAFARI-92	2.19±0.28
Czapiewski, 1999	Laboratory studies, domestic fires	10.7
	Field studies, domestic fires	7.1
Yonemura et al., 2002	Grass, laboratory studies	
	high burning efficiency	4.4–4.6
	low burning efficiency	13.1

ACPD

5, 10455–10516, 2005

Table 3. Summary of published emission ratios $\Delta CH_4/\Delta CO_2$.

	Comments	$\Delta CH_4/\Delta CO_2$ %
Crutzen et al., 1979	Forest fires	2.1
		(1.6–2.5)
		2.2
		(1.0–3.4)
Greenberg et al., 1984	Cerrado (grassland),	1.1
	average range	0.3–2.6
	Selva (tropical forest),	0.6
	average range	0.2–2.4
Crutzen et al., 1985	Cerrado	0.9 (0.3–2.6)
Cofer III et al., 1988	Chaparral	0.43
Lobert, 1989	Grass, straw, needles, laboratory study	1.1
Cofer et al., 1989	Forest fires	0.6
		(0.4–0.9)
Cofer III et al., 1990	Boreal forests	0.61
Bonsang et al., 1991	West Africa, DECAFE	0.54 (0.25–0.78)
Cofer III et al., 1991		(0.27–1.21)
Griffith et al., 1991		(1.1–1.6)
Ward et al., 1992	Boreal forests, flaming phase	0.61
	Smouldering phase	1.22
Kaufmann et al., 1992	Forests in Brasil (BASE-A)	0.3
Cofer III, 1993	Tropical fires	0.7
Hurst et al., 1993		0.39 (0.08–1.14)
Lacaux, 1995	Savanna, Westafrica, FOS/DECAFE	0.31
Bonsang et al., 1991, 1995	Savanna, Ivory Coast, January 1989, average	0.54±0.24
FOS/DECAFE	Flaming phase,	0.37±0.11
	Smoldering phase	0.78±0.20
Bonsang et al., 1995	Savanna, Ivory Coast, January 1991, average	0.60±0.43
FOS/DECAFE	Flaming phase,	0.42±0.16
	Smoldering phase	0.78±0.30
Hurst et al., 1996	Australian savanna	0.4
Andreae et al., 1996	Savanna South Africa, SAFARI	0.4
SAFARI	(mean of all savanna fires)	(0.31–0.42)
Koppmann et al., 1997	wild fire, mainly wood, SAFARI-92	1.03±0.17
Koppmann et al., 1997	Kruger National Park, SAFARI-92	0.28±0.07
Koppmann et al., 1997	Sugar cane fire #1, SAFARI-92	0.26±0.22
	Sugar cane fire #2, SAFARI-92	0.11±0.09
Czapiewski, 1999	Laboratory studies, domestic fires	1.3
	Field studies, domestic fires	0.8

ACPD

5, 10455–10516, 2005

Table 4. Summary of published emission ratios $\Delta\Sigma VOC/\Delta CO_2$.

	Comments	$\Delta\Sigma VOC/\Delta CO_2$ %
Greenberg et al., 1984	Cerrado (grassland),	1.2
	average range	0.4–2.8
	Selva (tropical forest),	1.1
	average range	0.3–3.4
Cofer III et al., 1988	Chaparral	4.1
Lobert, 1989	Grass, straw, needles	3.00
Cofer et al., 1989	Forest fires	0.66
		(0.4–1.2)
Cofer III et al., 1990	Boreal forests	0.67
Ward et al., 1992	Boreal forests, flaming phase	0.61
	Smouldering phase	1.15
Kaufmann et al., 1992	Forests in Brasil (BASE-A)	
Cofer III, 1993	Tropical fires	1.7
Lacaux, 1995	Savanna, Westafrica, FOS/DECAFE	0.70
Bonsang et al., 1991, 1995	Savanna, Ivory Coast, January 1989, average FOS/DECAFE	0.81±0.38
	Flaming phase	0.62±0.23
	Smoldering phase	0.77±0.46
Bonsang et al., 1995	Savanna, Ivory Coast, January 1991, average FOS/DECAFE	1.08±0.70
	Flaming phase	0.69±0.37
	Smoldering phase	1.08±0.30
Hurst et al., 1996	Australian savanna	0.99
Andreae et al., 1996	Savanna South Africa, SAFARI–92 (mean of all savanna fires)	0.6–1.0
Koppmann et al., 1997	wild fire, mainly wood, SAFARI-92	1.37±0.09
Koppmann et al., 1997	Kruger National Park, SAFARI-92	0.74±0.16
Koppmann et al., 1997	Sugar cane fire #1, SAFARI-92	0.39±0.29
	Sugar cane fire #2, SAFARI-92	0.17±0.07
Czapiewski, 1999	Laboratory studies, domestic fires	1.7
	Field studies, domestic fires	1.6

ACPD
5, 10455–10516, 2005

Table 5. Summary of published emission ratios of halogenated hydrocarbons relative to CO_2.

	CH_3Cl/CO_2	CH_3Br/CO_2	CH_3I/CO_2	CH_2Cl_2/CO_2	CH_3CCl_3/CO_2
Crutzen et al., 1979 Temperate forest	$(0.44–5.72)\times10^{-5}$				
Rasmussen et al., 1980 Wood	$(2.17–5.83)\times10^{-5}$				
Tassios and Packham, 1985 Eucalyptus	$(5.6–52.2)\times10^{-5}$				
Lobert et al., 1991 Lab studies	$(5.7–32.9)\times10^{-5}$				
Rudolph et al., 1995 Savanna	$(4.30\pm0.95)\times10^{-5}$			$(3.45\pm0.62)\times10^{-6}$	$(4.31\pm1.94)\times10^{-7}$
Andreae et al., 1996 Sugar cane	$(1.6–2.2)\times10^{-5}$	0.11×10^{-6}	0.09×10^{-6}		
Andreae et al., 1996 Kruger NP	$(9.2–10.6)\times10^{-5}$				
Blake et al., 1996	$(2.3–3.1)\times10^{-5}$				
	$CCl_4/CO2$	$CHCl_3/CO_2$	$C_2F_3Cl_3/CO_2$	C_2Cl_4/CO_2	C_2HCl_3/CO_2
Crutzen et al., 1979 Temperate forest					
Rasmussen et al., 1980 Wood					
Tassios and Packham, 1985 Eucalyptus					
Lobert et al., 1991 Lab studies					
Rudolph et al., 1995 Savanna	$(8.00\pm33.0)\times10^{-8}$	$(7.74\pm2.17)\times10^{-8}$	$(5.17\pm2.64)\times10^{-8}$	$(2.77\pm17.5)\times10^{-9}$	$(-3.83\pm7.66)\times10^{-7}$
Andreae et al., 1996 Sugar cane					
Andreae et al., 1996 Kruger NP					
Blake et al., 1996					

Table 6. Summary of published emission ratios of nitrogen containig compounds relative to CO_2.

	$\Delta NO_x/\Delta CO_2$	$\Delta NO_y/\Delta CO2$	$\Delta NH_3/\Delta CO_2$	$\Delta N_2O/\Delta CO_2$
Evans et al., 1977	$(0.4–1.6) \times 10^{-3}$			
Crutzen et al., 1985	1.9×10^{-3}			
	$(1.6–2.3) \times 10^{-3}$			
Hao et al., 1987	$(0.5–3.4) \times 10^{-3}$			
Andreae et al., 1988	1.5×10^{-3}			
	$(0.5–3.5) \times 10^{-3}$			
Cofer et al., 1989				
Chaparral fires				
flaming			$(0.14\pm0.02) \times 10^{-3}$	
smoldering			$(0.39\pm0.08) \times 10^{-3}$	
Cofer et al., 1989				
Boreal forest fires				
flaming			$(0.19\pm0.04) \times 10^{-3}$	
Lobert et al., 1989	1.7×10^{-3}			
Laboratory studies	$(1.65–1.92) \times 10^{-3}$			
Griffith et al., 1991	$(<0.9–1.7) \times 10^{-3}$			
Hurst et al., 1994	1.6×10^{-3}			
	$(0.2–4.1) \times 10^{-3}$			
Delmas et al., 1995				
FOS/DECAFE	0.14×10^{-2}	0.19×10^{-2}	0.057×10^{-3}	0.145×10^{-3}
range	$(0.8–2.3) \times 10^{-2}$	$(0.17–0.21) \times 10^{-2}$	$(0.023–0.10) \times 10^{-3}$	$(0.051–0.403) \times 10^{-3}$
Cofer et al., 1996				
SAFARI-92				
flaming phase			$(0.07\pm0.02) \times 10^{-3}$	
smoldering phase			$(0.14\pm0.02) \times 10^{-3}$	

ACPD
5, 10455–10516, 2005

Table 7. Emissions of total carbon and CO from various biomass burning sources.

Source	Biomass burned Tg (dry matter)/yr	Carbon released Tg/yr	CO emission ratio, %	CO emission Tg C/yr
Tropical forest	1260	567	10.9	62
Extratropical forest	1150	518	11.2	58
Savanna	3690	1661	6.2	103
Biomass fuel	1940	873	8.3	73
Charcoal	20	42	20.0	8
Agricultural waste in fields	850	383	7.2	28
Total	8910	4043	8.2	331

ACPD
5, 10455–10516, 2005